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Synthesis of DBpin Using Earth-abundant Metal Catalysis

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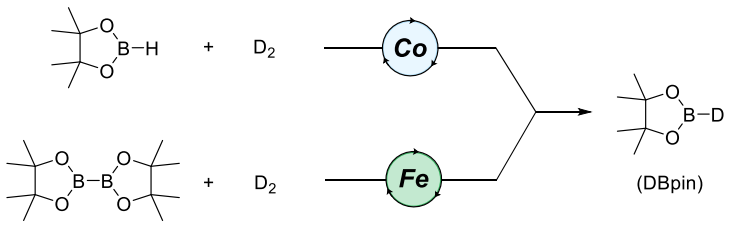

• Alkoxide Activation • Safe and Simple Procedure • High Isolated Yields • >99% Deuterium Incorporation

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Synthesis of DBpin Using Earth-abundant Metal Catalysis

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ABSTRACT

The synthesis of DBpin was achieved using (^{Et}BIP)$CoCl_2$ or (^{tBu}PNN)$FeCl_2$ as pre-catalysts activated with NaO^{t}Bu. (^{Et}BIP)$CoCl_2$ was used as a pre-catalyst for the hydrogen isotope exchange of HBpin with D_2, and (^{tBu}PNN)$FeCl_2$ for deuterogenolysis of B_2pin_2. The one-pot, tandem hydrogenolysis-hydroboration/deuterogenolysis-deuteroboration reaction of terminal alkenes could be catalysed by (^{tBu}PNN)$FeCl_2$ to give alkyl boronic esters.

1. Introduction

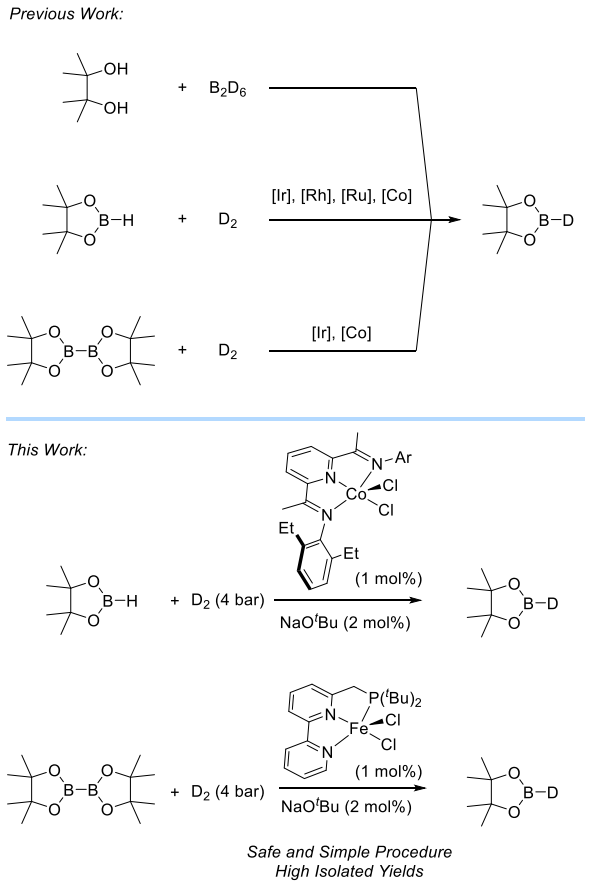
Deuterated compounds have found use across a wide range of applications from mechanistic analysis to pharmacokinetic studies. The strength of the C-D bond slows metabolism and can therefore facilitate lower pharmaceutical doses and numerous deuterated active pharmaceutical ingredients are currently undergoing clinical trials, with Deutetrabenazine having been fully approved by the FDA [1].

Boronic esters are ubiquitous in modern organic chemistry due to their functional group tolerance and broad applications [2–4]. Boronic esters are commonly prepared by the metal-catalysed hydroboration of alkenes and alkynes, with a wide range of transition metal and main group catalysts having been developed [5,6]. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (HBpin) has become a common reagent in organic synthesis, due to its stability and that of alkyl and aryl pincacolboronic esters [7]. The deutero-isotopologue, DBpin offers a simple means of deuterium-incorporation and has been commonly used for *in situ* reaction monitoring of reactive species, and allows for a B-H kinetic isotope effect to be determined [8–16].

The synthesis of HBpin was first reported by Knochel by reaction of $Me_2S{\cdot}BH_3$ with pinacol and distillation to give a high yield of HBpin [17]. A similar synthetic route has been commonly used to prepare DBpin, but requires the prior synthesis of B_2D_6 gas, which is toxic, pyrophoric, and requires a complex reaction setup [18]. DBpin has also been prepared by hydrogen isotope exchange of HBpin, however low deuterium incorporation is common, and forcing conditions can be needed. The first example of hydrogen isotope exchange of HBpin was reported by Perutz and co-workers using a rhodium catalyst, however the DBpin was not isolated from the reaction [19]. Further examples of hydrogen isotope exchange have been shown with iridium and ruthenium complexes [13,20], but only a single example has been reported using an Earth-abundant metal, a methyl-cobalt complex, which gave good deuterium incorporation at room temperature [8].

The deuterogenolysis of bis-(pincolato)borane (B_2pin_2) provides a synthetically simple route to DBpin, with high deuterium incorporation. The deuterogenolysis of B_2pin_2 was first demonstrated by Hartwig and Hall using an iridium catalyst, however due to low reactivity the reaction required multiple charges of D_2 over the period of 24 h [9]. Marder and Braunschweig demonstrated the hydrogenolysis of B_2pin_2 using a heterogenous catalyst [21]. Huang demonstrated the use of a PNN-ligated cobalt catalyst for the deuterogenolysis of B_2pin_2, with high reactivity and the generated DBpin could be used *in situ* for the deuteroboration of alkenes and alkynes using the same catalyst. $NaHBEt_3$ was required to activate the cobalt pre-catalyst [22].

We have previously demonstrated NaO^{t}Bu as an alternative to organometallic activators in Earth-abundant metal catalysis, thus we sought to extend this to the synthesis of DBpin [23]. Herein we report the use of Earth-abundant metal catalysts for the hydrogen isotope exchange of HBpin and deuterogenolysis of B_2pin_2 using bench stable pre-catalysts and NaO^{t}Bu as the activator to give DBpin with high deuterium incorporation and simple purification.

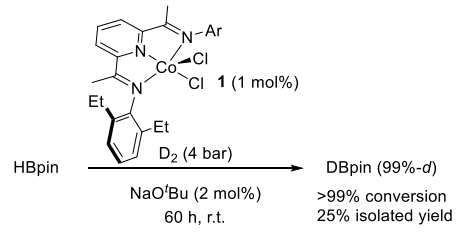


Scheme 1. Synthesis of 2-deutero-4,4,5,5-tetramethyl-1,3,2-dioxaboralane (DBpin) catalysed by transition metal complexes.

2. Results and discussion

2.1. Hydrogen Isotope Exchange of HBpin

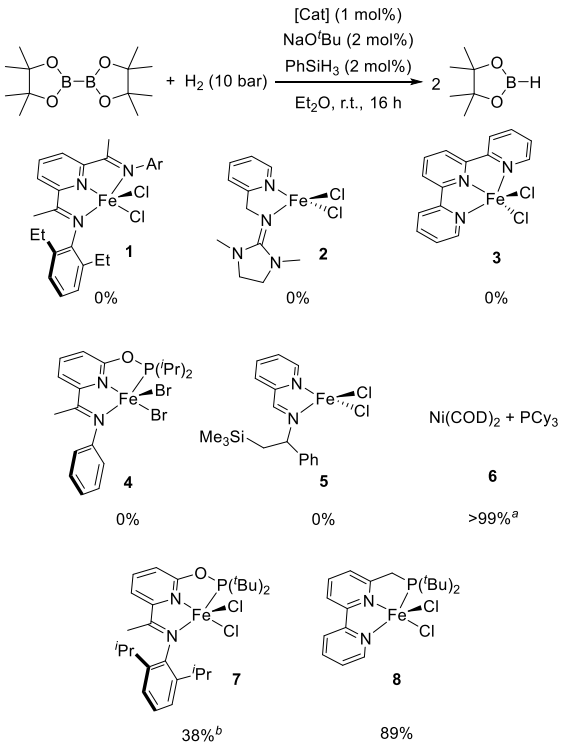
Chirik reported that the Co(I)-methyl complex, (^{Mes}BIP)CoCH$_3$, could catalyse hydrogen isotope exchange with HBpin, therefore we attempted to access this reactivity by *in situ* alkoxide activation from the parent Co(II) complex (^{Et}BIP)CoCl$_2$ [8]. We found that hydrogen isotope exchange occurred readily using (^{Et}BIP)CoCl$_2$ **1** as a catalyst and NaO^{t}Bu as an activator when the reaction was carried out in *neat* HBpin under D_2 (4 bar) giving excellent deuterium incorporation (99%-*d*) and conversion (>99%), but poor isolated yield (25%). Presumably when the reaction was removed from the D_2 atmosphere, the catalyst promoted the degradation of DBpin into redistribution products, such as B_2pin_3.



Scheme 2. Hydrogen isotope exchange of HBpin by (^{Et}BIP)CoCl$_2$ using NaO^{t}Bu as an activator.

2.2. Hydrogenolysis and deuterogenolysis of B_2pin_2

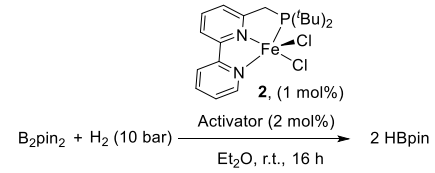
We next turned our attention to the hydrogenolysis of B_2pin_2. Various iron complexes were assessed, Milstein's PNN and Huang's PONN complexes [24,25], (^{tBu}PONN^{iPr})FeCl$_2$ **7** and (^{tBu}PNN)FeCl$_2$ **8** were found to give the only active catalysts using a combination of PhSiH$_3$ and NaO^{t}Bu for pre-catalyst activation (Scheme 3) [23]. We also found that Ni(COD)$_2$ in combination with PCy$_3$ gave excellent conversion [22].



Scheme 3. Hydrogenolysis of B_2pin_2 with various catalysts. Values listed are conversion by ^{11}B NMR. [a] Without PhSiH$_3$ and NaO^{t}Bu, with THF as the solvent. [b] 5 mol% catalyst loading used.

Using (^{tBu}PNN)FeCl$_2$ **8** we tested various organometallic activators as a performance comparison (Table 1) [23]. All organometallic activators were found to give significant amounts of B_2pin_3 along with other degradation products, as observed by ^{11}B NMR spectroscopy, and PhSiH$_3$ and NaO^{t}Bu remained the activator of choice.

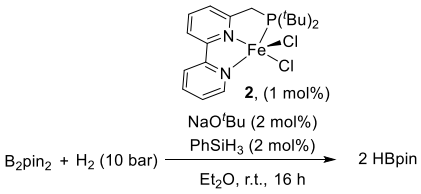
Table 1. Activator screen for the hydrogenolysis of B_2pin_2 by (^{tBu}PNN)FeCl$_2$. Conversion calculated from ^{11}B NMR.



Entry	Activator	Conversion (%)
1	NaO^{t}Bu + PhSiH$_3$	89
2	NaHBEt$_3$	37
3	EtMgBr	51
4	PhLi	81

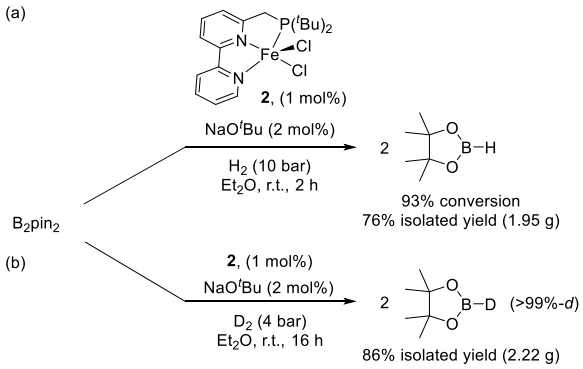
We then carried out a series of control reactions to ensure that the iron catalyst and activator were required. Interestingly, it was found the exogenous PhSiH$_3$ was not required to activate the pre-catalyst, with B_2pin_2 able to perform the same function (Table 2, entry 2). The same results were obtained regardless of whether the B_2pin_2 was purified by recrystallisation or not. We found that the reaction was complete in 2 hours.

Table 2. Control reactions. Conversion calculated from ^{11}B NMR.



Entry	Variation from standard conditions	Conversion (%)
1	None	89
2	No $PhSiH_3$	93
3	No NaO^tBu	0
4	Only (^{tBu}PNN)$FeCl_2$	0
5	Only NaO^tBu	0
6	Only ^{tBu}PNN Ligand	0
7	Time = 2 h	89

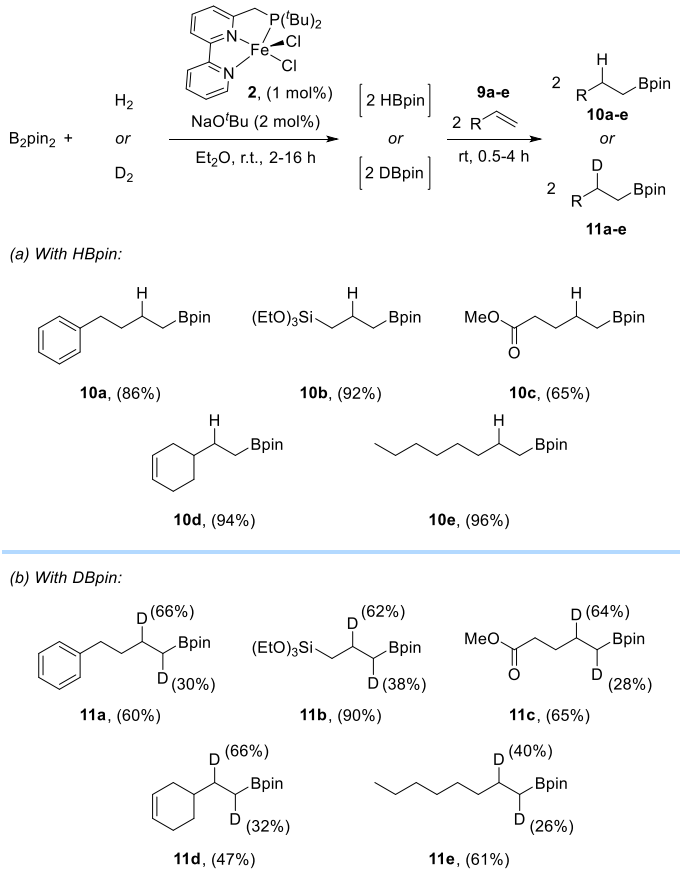
Having optimised hydrogenolysis conditions, we then set out to optimise the purification process. Et_2O was found to be the best reaction solvent, as it could easily be separated from the HBpin by distillation to give good isolated yield (76%) on gram scale. With optimised conditions for hydrogenolysis, we next sought to apply this reaction to the preparation of DBpin. Deuterogenolysis was found to be much slower than hydrogenolysis, presumably due to a kinetic isotope effect and a lower reaction pressure, therefore, the reaction time was extended to 16 hours. This gave DBpin in high isolated yield (86%) on gram-scale with >99%-*d* incorporation.



Scheme 4. (a) Optimised hydrogenolysis of B_2pin_2. (b) Optimised deuterogenolysis of B_2pin_2.

2.3. One-pot tandem hydrogenolysis-hydroboration and deuterogenolysis-deuteroboration of B_2pin_2

As (^{tBu}PNN)$FeCl_2$ is also reported to be a highly efficient hydroboration catalyst [26], we trialed a one-pot hydrogenolyis-hydroboration using the HBpin that was formed *in situ*. This hydroboration showed functional group tolerance to siloxanes (**10b**), esters (**10c**), and internal alkenes (**10d**) (Scheme 5, a). We extended this tandem reaction to the deuteroboration of terminal alkenes (Scheme 5, b). Presumably due to a significant kinetic isotope effect using DBpin the yields were lower than the analogous protio equivalent for all substrates. Deuterium incorporation was observed at both the terminal and internal position indicating the catalyst is operating by reversible hydrometallation of the alkene. No deuterium incorporation was observed at the internal alkene of a diene (**10d**), suggesting the hydrometallation is chemoselective for terminal alkenes (Scheme 5, b).



Scheme 5. (a) Scope of iron-catalysed one-pot hydrogenolysis-hydroboration of terminal alkenes. (b) Scope of iron-catalysed one-pot deuterogenolysis-deuteroboration of terminal alkenes. Deuterium incorporation determined by integration of the residual signal in the ^1H NMR spectrum.

3. Conclusions

We have successfully demonstrated the use of cobalt- and iron-catalysis for the synthesis of DBpin with high deuterium incorporation and isolated yield, using either hydrogen isotope exchange or deuterogenolysis. The one-pot tandem hydrogenolysis-hydroboration and deuterogenolysis-deuteroboration were also developed and applied to terminal alkenes.

4. Experimental section

4.1 General

Reaction setup: All reactions were performed in oven (185 ºC) and/or flame dried glassware. All glassware was cleaned using base (KOH, ^{i}PrOH) and acid (HCl_{aq}) baths. All reported reaction temperatures correspond to ambient room temperature, which was approximately 20 ºC.

NMR spectroscopy: ^1H, ^2D, ^{13}C and ^{11}B spectra were recorded on Bruker Avance III 400 and 500 MHz; Bruker PRO 500 MHz; Bruker Avance I 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm). ^1H and ^{13}C NMR spectra were referenced to the residual solvent peak ($CDCl_3$: 7.26 ppm). Multiplicities are indicated by app. (apparent), br. (broad), s (singlet), d (doublet), t (triplet), q (quartet), quin. (quintet), sext. (sextet), sept. (septet), non. (nonet). Coupling constants, J, are

reported in Hertz and rounded to the nearest 0.1 Hz. Integration is provided and assignments are indicated.

Chromatography: Column chromatography was carried out on a Teledyne ISCO CombiFlash NextGen 300+ using RediSep Rf Gold normal phase silica flash columns (12, 25, 40, or 80 g; 20-40 microns). Substrates were purified using 40/60 petroleum ether and EtOAc on a gradient of 100:0 to 0:100 with flow rates of 10-110 mL min^{-1} depending on the size of column and ΔR_f.

Mass Spectrometry: Mass spectrometry (MS) was performed by the University of Edinburgh, School of Chemistry, Mass Spectrometry Laboratory. High resolution mass spectra were recorded on a VG autospec, or Thermo/Finnigan MAT 900, mass spectrometer. Electron Impact (EI^+) spectra were performed at 70 eV using methane as the carrier gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyzer. Chemical Ionization (CI^+) spectra were performed with methane reagent gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyzer. Electrospray Ionization (ESI^+) spectra were performed using a time-of-flight (TOF) mass analyzer. Data are reported in the form of m/z (intensity relative to the base peak = 100).

Chemicals: All reagents and were purchased from Sigma Aldrich, Alfa Aesar, Acros organics, Tokyo Chemical Industries UK, Fluorochem and Apollo Scientific without further purification. Sodium *tert*-butoxide (97%) was purchased from Sigma Aldrich (UK). B_2pin_2 was purchased from Fluorochem and recrystallised before use. All cobalt and iron species were prepared according to reported procedures [23,24,26–28].

4.2. Preparation of DBpin with (^{Et}BIP)$CoCl_2$

Under argon, to an autoclave was added (^{Et}BIP)$CoCl_2$ (0.14 mmol, 76 mg), and NaO^{t}Bu (0.28 mmol, 30 mg). HBpin (2.0 mL, 14 mmol) was added dropwise *n.b. exothermic*. The vessel was sealed, flushed with D_2, then pressurised with D_2 (4 bar). The reaction was left to stir at room temperature for 36 h, then the flush/pressurise cycle was repeated, and the reaction was left to stir for another 24 h. The DBpin was distilled *in vacuo* (25 °C, 0.1 mbar), to give DBpin (0.50 g, 25%, 99%-d) as a colourless oil. The deuterium incorporation was determined by integration of the residual HBpin signal. ^{1}H NMR (500.12 MHz, $CDCl_3$): 1.27 (12H, s, CH_3). ^{11}B NMR (128.34 MHz, $CDCl_3$): 28.2 (s br), ^{13}C NMR (125.77 MHz, $CDCl_3$) 25.0, 83.4. ^{2}D NMR (76.75 MHz, toluene) 4.15 (br m). Analytical data were in accordance with those previously reported [22].

4.3. Hydrogenolysis of B_2pin_2

B_2pin_2 (10 mmol, 2.54 g), ($^{t\text{Bu}}$PNN)$FeCl_2$ (0.1 mmol, 44 mg) and NaO^{t}Bu (0.2 mmol, 19 mg) were dissolved in Et_2O (10 mL) in an autoclave. The vessel was purged with H_2 then pressurised with H_2 (10 bar). This was left to stir for 2 hours, then the pressure was released. The reaction mixture was distilled at atmospheric pressure to remove Et_2O (60 °C). The HBpin was distilled *in vacuo* (25 °C, 0.1 mbar) giving HBpin (1.95 g, 76%) as a colourless oil. ^{1}H NMR (500.12 MHz, $CDCl_3$): 1.22 (12H, s, CH_3), 3.81 (1H, 1:1:1:1 q, J = 171.7 Hz). ^{11}B NMR (128.34 MHz, $CDCl_3$): 28.2 (d, J = 174.9 Hz), ^{13}C NMR (125.77 MHz, $CDCl_3$) 25.0, 83.3. Analytical data were in accordance with those previously reported [22].

4.4. General procedure for one-pot hydroboration of terminal alkenes.

B_2pin_2 (0.500 mmol, 127 mg), ($^{t\text{Bu}}$PNN)$FeCl_2$ (0.005 mmol, 2.2 mg), and NaO^{t}Bu (0.01 mmol, 0.8 mg) were dissolved in Et_2O (0.5 mL) in an autoclave. The vessel was purged with H_2 then pressurised with H_2 (10 bar). The reaction was stirred for 2 hours, then the pressure was released and the vessel transferred into a glovebox. Alkene (1.00 mmol) was added, and the reaction left to stir for 30 mins. The solvent was removed *in vacuo* and the residue purified by flash column chromatography on silica (with a mixture of 40/60 petroleum ether and diethyl ether). Volatiles were removed *in vacuo* to give the alkyl boronic ester.

4.5. Deuterogenolysis of B_2pin_2

B_2pin_2 (10.0 mmol, 2.54 g), ($^{t\text{Bu}}$PNN)$FeCl_2$ (0.10 mmol, 44 mg) and NaO^{t}Bu (0.20 mmol, 19 mg) were dissolved in Et_2O (10 mL) in an autoclave. The vessel was purged with D_2 then pressurised with D_2 (10 bar). This was left to stir for 16 hours, then the pressure was released. The reaction mixture was distilled at atmospheric pressure to remove Et_2O (60 °C). The DBpin was distilled *in vacuo* (25 °C, 0.1 mbar), to give DBpin (2.22 g, 86%, >99%-*d*) as a colourless oil. ^{1}H NMR (500.12 MHz, $CDCl_3$): 1.27 (12H, s, CH_3). ^{11}B NMR (128.34 MHz, $CDCl_3$): 28.2 (s br), ^{13}C NMR (125.77 MHz, $CDCl_3$) 25.0, 83.4. ^{2}D NMR (76.75 MHz, toluene) 4.15 (br m). Analytical data were in accordance with those previously reported [22].

4.6. General procedure for one-pot deuteroboration of terminal alkenes.

B_2pin_2 (0.500 mmol, 127 mg), ($^{t\text{Bu}}$PNN)$FeCl_2$ (0.005 mmol, 2.2 mg), and NaO^{t}Bu (0.01 mmol, 0.8 mg) were dissolved in Et_2O (0.5 mL) in an autoclave. The vessel was purged with D_2 then pressurised with D_2 (4 bar). This was left to stir for 16 hours, then the pressure was released and the vessel transferred into a glovebox. Alkene (1.00 mmol) was added, and the reaction left to stir for 4 hours. The solvent was removed *in vacuo* and the residue purified by flash column chromatography on silica (with a mixture of 40/60 petroleum ether and diethyl ether). Volatiles were removed *in vacuo* to give the deutero alkyl boronic ester.

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